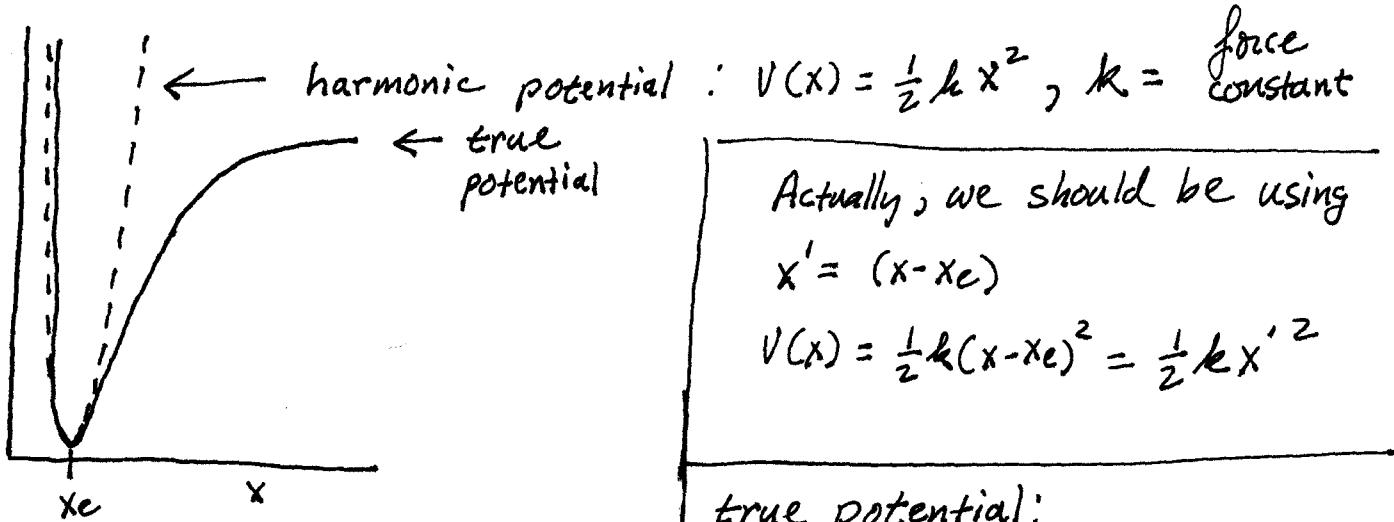


## Chpt. 7 - Vibrations + rotations

translation - particle in box

rotation - rigid rotor

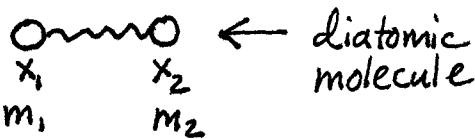
vibration - harmonic oscillator



Actually, we should be using

$$x' = (x - x_e)$$

$$V(x) = \frac{1}{2} k (x - x_e)^2 = \frac{1}{2} k x'^2$$



center of mass coordinates

for vibration what matters  
is the separation between  
the atoms

reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

true potential:

$$V(x) = V(x_e) + \left. \frac{dV}{dx} \right|_{x_e} (x - x_e) + \frac{1}{2} \left. \frac{d^2 V}{dx^2} \right|_{x_e} (x - x_e)^2 + \frac{1}{6} \left. \frac{d^3 V}{dx^3} \right|_{x_e} (x - x_e)^3 + \dots$$

choose  $V(x_e)$  to be the zero  
of energy

$$\left. \frac{dV}{dx} \right|_{x=x_e} = 0$$

$$V(x) = \frac{1}{2} \left. \frac{d^2 V}{dx^2} \right|_{x_e} (x - x_e)^2 + \dots$$

$$= \frac{1}{2} k (x - x_e)^2 + \dots$$

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$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi = E\psi$$

Note:  $e^{-\frac{1}{2}\alpha x^2}$  is a solution

$$\frac{d}{dx} e^{-\frac{\alpha}{2}x^2} = -\alpha x e^{-\frac{\alpha}{2}x^2}$$

$$\frac{d}{dx} \left[ -\alpha x e^{-\frac{\alpha}{2}x^2} \right] = (-\alpha + \alpha^2 x^2) e^{-\frac{\alpha}{2}x^2}$$

Do you see why this solves the equation?

$e^{+\frac{\alpha}{2}x^2}$  also solves the differential equation. But we reject it. Why?

The general form of the wavefunction is

$$\psi_n = A_n H_n(\alpha^{1/2}x) e^{-\frac{\alpha}{2}x^2}, \quad n=0,1,2,\dots$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

$$A_n = \frac{1}{\sqrt{2^n n!}} \left( \frac{\alpha}{\pi} \right)^{1/4}$$

$$\psi_0 = \left( \frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha}{2}x^2}$$

$$\psi_1 = \left( \frac{4\alpha^3}{\pi^2} \right)^{1/4} x e^{-\frac{\alpha}{2}x^2}$$

$$\psi_2 = \left( \frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) e^{-\frac{\alpha}{2}x^2}$$

$$\psi_3 = \left( \frac{\alpha^3}{9\pi} \right)^{1/4} (2\alpha x^3 - 3x) e^{-\frac{\alpha}{2}x^2}$$

$H_n(\alpha^{1/2}x)$  : hermite polynomials

$\psi_0, \psi_2, \psi_4, \dots$  even

$\psi_1, \psi_3, \psi_5, \dots$  odd

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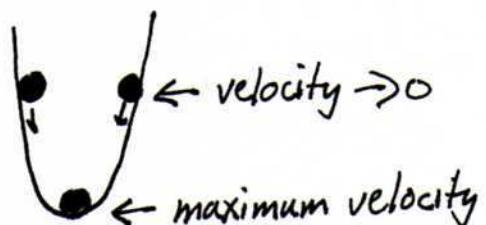
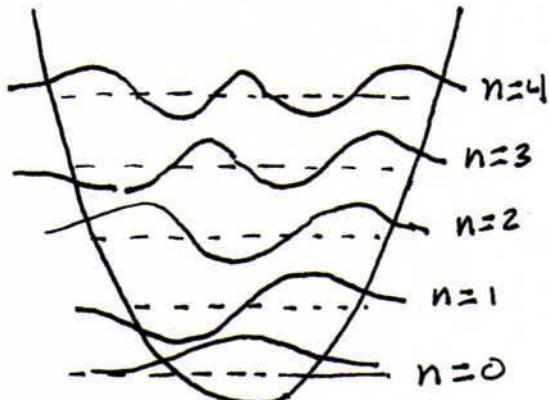
$$E_n = \hbar\sqrt{\frac{k}{m}}(n + \frac{1}{2}) = \hbar\omega(n + \frac{1}{2}) = h\nu(n + \frac{1}{2}), n=0,1,2,\dots$$

quantization due to requiring  $\psi \rightarrow 0$  as  $x \rightarrow \infty$

$$\langle E_{KE} \rangle = \langle E_{PE} \rangle = \frac{h\nu}{2}(n + \frac{1}{2})$$

as  $n$  becomes large, there is a high probability of finding the oscillator near the classical turning points

Similar situation for the classical oscillator



$$\langle 0 | x | 0 \rangle = 0$$

$$\langle 1 | x | 1 \rangle = 0$$

$$\langle 1 | 0 \rangle = 0$$

$$\langle 1 | x | 0 \rangle \neq 0$$

$$\langle n | \hat{A} | m \rangle = \int \psi_n^* \hat{A} \psi_m dx$$

The integral  $\langle n | x | 0 \rangle$  is the transition moment for going from state  $\psi_0$  to  $\psi_n$ .

$$\text{Transition probability} \propto |\langle n | x | 0 \rangle|^2$$

integral nonzero only if  $n=1$ .

Later we will see that it is also essential that the dipole moment is changing